Preface

Diffusion is a fundamental process which plays a crucial role in many processes occurring in nature. It is governed by the Fickian laws of diffusion. The laws of diffusion explain how diffusive flux is related to the concentration gradient. However, diffusion occurs even when there is no concentration gradient. Chapter 1 introduces diffusion and related concepts such as random walk, Brownian motion, etc. Present understanding with relation to ionic conduction and diffusion in polar solvents and the anomalies observed in the variation of ionic conductivity with ionic radii has also been discussed. Walden's rule states that the product of limiting ionic conductivity and viscosity is constant for a given ion in different solvents and it is inversely proportional to ionic radius in a given solvent. However, experimental observations indicate that in a given solvent limiting ionic conductivities show an increase followed by a decrease with increase in ionic radii. This is often referred to as the breakdown of Walden's rule. Several theories have been proposed in the past to explain the breakdown in Waldens rule. Solvent-berg model, continuum based theories and microscopic theories are some of theories that have been proposed. These theories are discussed briefly. The limitations in these theories are also outlined. There are several computer simulation investigations of ions in water and these are discussed. Also described is diffusion of hydrocarbons in zeolites. Various interesting observations such as window effect, nest effect, single file diffusion and the levitation effect are discussed.

In Chapter 2, we have analysed the experimental ionic conductivity data as a function of the ionic radius for monovalent cations and anions in aqueous solution. Molecular dynamics simulations on LiCl and CsCl dissolved in water are also reported. The results suggest

that the activation energy is responsible for the anomalous dependence of ionic conductivity on ionic radii. It is seen that ions with high conductivity posses low activation energy. The reason for the variation of activation energy with ionic radii are explained in terms of Derouane's mutual cancellation of forces or levitation effect. This provides an alternative to the existing theories.

Experimental limiting ionic conductivity, λ^0 of different alkali ions in water shows markedly different dependences on pressure. Existing theories such as that of Hubbard-Onsager are unable to explain this dependence on pressure of the ionic conductivity for all ions. Experimental ionic conductivity data shows that smaller ions such as Li^+ exhibit a monotonic increase in λ^0 with pressure. Intermediate sized ions such as K^+ exhibit an increase in λ^0 followed by a decrease at still higher pressures. Larger ions such as Cs^+ exhibit a monotonic decrease in λ^0 with increase in pressure. In the present thesis, we have explored this intriguing behaviour shown by alkali ions in water in the next few chapters.

In Chapter 3, we report molecular dynamics investigation of potassium chloride solution (KCl) at low dilution in water at several pressures between 1 bar and 2 kbar. Two different potential models have been employed. One of the models successfully reproduces the experimentally observed trend in ionic conductivity of K^+ ion in water over 0.001-2 kbar range at 298K. We also propose a theoretical explanation, albeit at a qualitative level, to account for the dependence of ionic conductivity on pressure in terms of the previously studied Levitation Effect. A number of properties of the solvent in the hydration shell are also reported.

In Chapter 4, residence times of water in the solute and water hydration shell are reported for KCl in water as a function of pressure. Two different approaches – Impey, McDonald and Madden's approach as well as the recently proposed stable state picture (SSP) of Laage and Hynes yield somewhat different values for the residence times. The

latter suggests that the hydration shell is more labile. As pressure is varied, the analysis suggests drastic changes in the hydration shell around water and little or no change in the hydration shell of the ions at higher pressures. The residence times τ_{IMM} as well as τ_{SSP} show a decrease with increase in pressure upto 1.5 kbar and a small increase beyond this pressure. This correlates with the dependence of the ionic conductivity of potassium ion on pressure. Similar correlation is also seen for chloride ion between ionic conductivity and residence time in hydration shell. However, no such correlation is seen in the case of water. We also report variation of residence time as a function of t^*, the minimum time that a water has to leave the hydration shell to be excluded from it.

In Chapter 5, a molecular dynamics study of LiCl dissolved in water is reported at several pressures between 1 bar and 4 kbars at 240K. Structural properties such as radial distribution function, distribution of the angle between ion-oxygen and dipole vector of water in the hydration shell, angle between ion-oxygen and OH vector, oxygen-ion-oxygen angle for water in the hydration shell, mean residence times by two different approaches are reported. Self-diffusivity of both Li^+ and Cl^- exhibit an increase with pressure in agreement with the experimentally observed trend. We also report the velocity autocorrelation function as a function of pressure. We show that the changes in these can be understood in terms of the levitation effect. For the first time we report the self part of the intermediate scattering function, $F_s(k,t)$, at different pressures. These show for Li+ at small wavenumber k, a bi-exponential decay with time at low pressures. At higher pressures when the ionic conductivity is high, $F_s(k,t)$ exhibits a single exponential decay. We also report wavenumber dependence of the ratio of the full width at half maximum to $2Dk^2$. These changes in these properties can be accounted for in terms of the levitation effect. The changes in the void structure of water with pressure plays a crucial role in the changes in ionic conductivity of both the ions.

In Chapter 6, a detailed molecular dynamics study of self-diffusivity of model ions in water is presented as a function of pressure. First, we have obtained the dependence of self-diffusivity on ionic radius for both cations and anions by varying the radius of the ion, r_{ion}. Self-diffusivity exhibits an increase with ionic radius when r_{ion} is small and reaches a maximum at some intermediate value, r_{ion}^{max}, before decreasing with increase in r_{ion} for $r_{ion} > r_{ion}^{max}$. The velocity autocorrelation function for different sizes of cations as well as anions suggest that the ion with maximum self-diffusivity has facile motion with little back scattering. These trends can be understood in terms of the levitation effect which relates the dependence of self-diffusivity on ionic radius to the bottleneck radius of the pore network provided by the solvent or water. The ratio ζ, defined as the full width at half maximum of the self part of the dynamic structure factor at wavenumber k to its value ($2Dk^2$) at $k = 0$ is seen to increase with k for ions far away from the diffusivity maximum while a decrease with k is observed for ions closer to the diffusivity maximum. Calculations have also been carried out at pressures of 0.001, 2 and 4 kbars to obtain the variation of ionic conductivity with pressure for model ions of several different sizes. It is shown that for small ions ($r_{ion} < r_{ion}^{max}$), self-diffusivity increases with pressure or exhibits an increase followed by a decrease. In contrast, we show that whenever ionic radius is large, ($r_{ion} > r_{ion}^{max}$), a decrease in self-diffusivity with increase in pressure is seen. We suggest that there is a relation between the dependence of self-diffusivity on ionic radius and its dependence on pressure. The nature of this relationship arises through the levitation effect. Increase in pressure leads to decrease in the bottleneck radius, thus increasing the levitation parameter. For small ions ($r_{ion} < r_{ion}^{max}$), this will lead to increase in diffusivity whereas for large ions ($r_{ion} > r_{ion}^{max}$) this will lead to decrease in diffusivity. For small ions ($r_{ion} < r_{ion}^{max}$), the increase in pressure leads to lowered back scattering in the velocity autocorrelation function. In contrast to this, for large ions ($r_{ion} \geq r_{ion}^{max}$), any increase in pressure leads to increase in back scattering in the velocity

autocorrelation function. For the 1.7 Å anion, the ratio ζ is seen to exhibit a minimum at intermediate k and increase with k at large k for 0.001 kbar pressure. This changes to a less pronounced minimum at 2 kbars and by 4 kbars to a nearly monotonically decreasing function of k. These changes suggest, in agreement with the predictions of the levitation effect, the approach of the bottleneck radius to values similar to that of the ionic radius of 1.7 Å on increasing pressure to 4 kbars. Thus, this work offers an unification in our understanding of the dependence of ionic conductivity on ionic radius and pressure. It is seen that when the ionic radius is varied the numerator of the expression for levitation parameter is varied whereas by varying the pressure, the denominator is varied.

The variation of diffusivity with density of the host medium and degree of disorder of the host medium is explored in Chapter 7. The system consists of a binary mixture of a relatively smaller sized solute (whose size is varied) and a larger sized solvent interacting via Lennard-Jones potential. Calculations have been performed at three different reduced densities of 0.7, 0.8 and 0.933. These simulations show that diffusivity exhibits a maximum for some intermediate size of the solute when the solute diameter is varied. The maximum is found at the same size of the solute at all densities which is at variance with the prediction of the levitation effect. In order to understand this anomaly, we have carried out additional simulations in which we have varied the degree of disorder at constant density and find that the diffusivity maximum gradually disappears with increase in disorder. We have also carried out simulations in which we have kept the degree of disorder constant but changed only the density. We find that the maximum in diffusivity is now seen to shift to larger distances with decrease in density. In these simulations we have characterized the disorder by constructing the minimal spanning tree. These results are in excellent agreement with the predictions of the levitation effect. They suggest that the effect of disorder is to shift the maximum in diffusivity towards smaller solute radius while that of the decrease in

density is to shift it towards larger solute radius. Thus, in real systems where the degree of disorder is lower at higher density and vice versa, the effect due to density and disorder have opposing influences. These are confirmed by the changes seen in the velocity autocorrelation function, self part of the intermediate scattering function and activation energy.

In Chapter 8 we report a molecular dynamics study of the dependence of diffusivity of the cation on cation radii in molten superionic salt containing iodine ion. In this study, we have employed modified Parinello-Rahman-Vashistha interionic pair potential proposed by Shimojo et al (F. Shimojo and M. Kobayashi, J. Phys. Soc. Jpn 60, 3725 (1991)). Our results suggest that the diffusivity of the cation exhibits an increase followed by a decrease as the ionic radius is increased. Several other properties like velocity auto correlation function, intermediate scattering function, activation energy are reported.

The next two chapters deal with diffusion of hydrocarbon isomers containing aromatic moiety. Chapter 9 reports structure, energetics and dynamic properties of the three isomers of trimethyl benzene in β-zeolite. Monte Carlo and molecular dynamics simulations have been performed at 300K. Of the three isomers, it is observed that 1,2,4-trimethyl benzene(124 TMB) shows fast dynamics inside the channels of β-zeolite. It is seen that both translational and rotational diffusivities are in the order D (124 TMB) $>$ D (123 TMB) $>$ D (135 TMB). 124 TMB seems to perform jumps between perpendicular channels more frequently whereas 123 and 135 isomers experience more hindrance to these jumps. It is also shown that there is a lower energetic barrier for 124 TMB across the window that separates two perpendicular channels in β-zeolite. Reorientational correlation functions suggest that reorientation of C_6 axis (axis perpendicular to the plane of the phenyl ring) is highly restricted in case of 135 TMB. Reorientation of C_2 axis (axis on the plane of the phenyl ring) seems to be more facile than that of C_6 axis in case of both 123 TMB and 135

TMB. And interestingly, C_6 and C_2 axis reorientations are equally facile in case of 124 TMB.

Chapter 10 presents molecular dynamics simulation results carried out on an equimolar binary mixture of cumene (isopropyl benzene) and pseudo-cumene (1,2,4-trimethyl benzene) in zeolite-NaY at four different temperatures. We compare different structural, energetic and dynamic properties of cumene and pseudo-cumene in zeolite-NaY. Our results suggest that both translational and rotational diffusivities are higher for cumene as compared to pseudo-cumene. Potential energy landscapes show that there is an energetic barrier for diffusion past the 12 MR window plane that separates two neighboring super cages. Such an energetic barrier is large for pseudo-cumene (3 kJ/mol) as compared to that of cumene (1.5 kJ/mol). Activation energies corresponding to both translational and rotational diffusion suggest that pseudo-cumene encounters larger energetic barriers for both translation and rotation as compared to cumene. Reorientational correlation functions suggest that reorientation of C_2 axis is more facile than that of C_6 axis in case of both cumene and pseudo-cumene. Activation energies corresponding to reorientational relaxations suggest that C_6 axis encounters larger energetic barriers as compared to C_2 axis in case of both cumene and pseudo-cumene.

Chapter 11 discusses the main conclusions of the thesis and directions for future work.